AIP Journal of Applied Physics

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Citation: Journal of Applied Physics **89**, 5919 (2001); doi: 10.1063/1.1368397
View online: http://dx.doi.org/10.1063/1.1368397
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/89/11?ver=pdfcov
Published by the AIP Publishing

Equilibrium and relaxation of particulate charge in fluorocarbon plasmas

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(Received 16 November 2000; accepted for publication 5 March 2001)

Charging of micron-size particulates, often appearing in fluorocarbon plasma etching experiments, is considered. It is shown that in inductively coupled and microwave slot-excited plasmas of C_4F_8 and Ar gas mixtures, the equilibrium particle charge and charge relaxation processes are controlled by a combination of microscopic electron, atomic (Ar^+ and F^+), and molecular ion (CF_3^+, CF_2^+, and CF^+) currents. The impact of molecular ion currents on the particulate charging and charge relaxation processes is analyzed. It is revealed that in low-power (<0.5 kW) microwave slot-excited plasmas, the impact of the combined molecular ion current to the total positive microscopic current on the particle can be as high as 40%. The particulate charge relaxation rate in fluorocarbon plasmas appears to exceed $10^8\ s^{-1}$, which is almost one order of magnitude higher than that from purely argon plasmas. This can be attributed to the impact of positive currents of fluorocarbon molecular ions, as well as to the electron density fluctuations with particle charge, associated with electron capture and release by the particulates.
[DOI: 10.1063/1.1368397]

I. INTRODUCTION

Purity of thin films is a key factor in many industrial applications, including semiconductor manufacturing, hard wear-resistant coatings, optical emitters, highly transparent films, etc. However, in many plasma-assisted thin film processes clouds of fine particles adversely affecting the efficiency of the process and film quality have frequently been reported.[1] In plasma enhanced chemical vapor deposition systems the fine crystallites normally originate as a result of gas phase reactions such as homogeneous or heterogeneous nucleation, and grow to detectable size by agglomeration and accretion.[2,3] In etching plasmas, dusts can also be created by release of substrate and film material into an adjacent plasma.[4] In plasma sputtering processes, the main mechanism of particulate formation is the gas-phase condensation of the sputtered material.[5] The size of particulates typically varies from tens of nanometers to tens of microns.[1] Thus, the fallout of dusts onto the substrate can produce unrecoverable defects and be a limiting factor in microstructuring of semiconductor wafers.[6]

Meanwhile, the fine particles almost instantly collect highly mobile plasma electrons, acquire large negative charge, and, affecting the overall charge neutrality and potential distribution in the plasma, modify the ion flows onto the substrate, and hence, the processing conditions. The other adverse effects include plasma instabilities due to modification of the ionization-recombination balance, which can be followed by mode jumps and even discharge disruption.[7] The charge proportion residing on the particles $\chi_d = n_d|Z_d|/\Sigma_{(j)} n_{(j)}$, where n_d and Z_d are the average particle number density and charge in units of electron charge, and $n_{(j)}$ is a number density of ionic species, respectively, is a key parameter that characterize the overall effect of contamination on the discharge.[8] The charge Z_d is controlled by a dynamic balance of microscopic electron and ion currents onto an individual particle.[9,10] The fluctuations of electron and ion currents results in dust charge variation, which relaxes within a time scale $t_{relax} \sim \nu_{ch}^{-1}$, where ν_{ch} is a dust charge relaxation rate.[9,10]

In this article, we consider the charging of micron-size particulates in fluorocarbon plasmas frequently used for ultrafine, highly efficient, and selective etching of dielectric materials.[11,12] We demonstrate that in plasmas of fluorocarbon-argon gas mixtures, used in etching experiments,[13] molecular ions CF^+, CF_2^+, and CF_3^+ significantly contribute to the particulate charging and charge relaxation process. We also improve the conventional charging model by accounting for the variations of background electron number density, which inevitably accompanies the particle charge variation. This factors result in enhanced, typically higher than $10^8\ cm^{-3}$, charging rates of micron-size particles.

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The article is organized as follows. In Sec. II, the problem and basic assumptions are formulated. Equilibrium charge of micron-size particles, effect of electron/ion temperatures, and contribution of fluorocarbon molecular ions are investigated in Sec. III. In Sec. IV, the charge relaxation process is studied. The implications and limitations of the present investigation are outlined in Sec. V. The article ends with Conclusion, where the summary of the results obtained and perspectives for future work are given.

II. FORMULATION

We consider the plasma generated in the gas mixture of octafluorocyclobutane (c-C_4F_8) and argon conventionally used for highly selective etching of silicon substrates.[11–14] Due to the overwhelming complexity of fluorocarbon-argon plasmas, the actual composition of the ions and radicals depends on many factors, including the kind of plasma source, the way power is coupled to the plasma, operating pressure, and gas inlet (proportions of C_4F_8 and Ar). In the process of etching, molecular species C_4F_8 almost completely dissociate into smaller ionic (superscript ''+'') and radical (superscript ''0'') fragments, such as $CF_3^{(0,+)}$, $CF_2^{(0,+)}$, $CF^{(0,+)}$, $F^{(0,+)}$, $C_3F_5^{(0,+)}$, $C_2F_4^{(0,+)}$, $C_3F_3^{(0,+)}$, $C^{(0,+)}$, etc..[14,15] To be specific, we limit our consideration to experiments on silicon wafer etching in 2.45 GHz microwave slot-excited (MSE) and 13.56 MHz inductively coupled plasma (ICP) sources.[13] In particular, MSE plasmas generated in 10% C_4F_8 and 90% Ar mixture at 2.66 Pa pressure feature dominant Ar^+, CF^+, CF_2^+, and CF_3^+ ion components in a wide range of rf input powers. Proportions of other ions, such as the fluorine ion, appear to be much lower. In inductively coupled plasmas, typically sustained by higher input powers, the proportion of argon ions is higher. The tendency of dominating, among other ionic species, of CF^+, CF_2^+, and CF_3^+ ions still persists.[13] We therefore assume that the plasma of C_4F_8 and Ar gas mixture consists of electrons, Ar^+, CF^+, CF_2^+, CF_3^+, and F^+ ions.

The particulates of an average radius a are assumed uniformly distributed through the plasma volume and separated from each other by $d \gg a$, where $a < r_{\mathrm{De}}$. Here, d is an interparticle distance, and r_{De} is the electron Debye length. The overall charge balance in the plasma is thus modified so that

$$\Sigma_{(j)} n_{(j)} = n_e + |Z_d| n_d , \tag{1}$$

where n_e is the electron density, and

$$\Sigma_{(j)} n_{(j)} = n_{\mathrm{Ar}^+} + n_{\mathrm{CF}_3^+} + n_{\mathrm{CF}_2^+} + n_{\mathrm{CF}^+} + n_{\mathrm{F}^+}$$

is the combined number density of positive ions, which neutralize the negative charge of electrons and particulates.

The charging process is controlled by microscopic electron $I_e(q_d)$ and combined ion $\Sigma_{(j)} I_{(j)}(q_d)$ currents, which are in turn functions of the dust charge q_d. Any imbalance between these currents yields particle charge variation, described by

$$\frac{dq_d}{dt} = I_e(q_d) + \Sigma_{(j)} I_{(j)}(q_d), \tag{2}$$

where $q_d = -|Z_d| e$ is a negative dust charge, and

$$\Sigma_{(j)} I_{(j)}(q_d) = I_{\mathrm{Ar}^+}(q_d) + I_{\mathrm{CF}_3^+}(q_d) + I_{\mathrm{CF}_2^+}(q_d) + I_{\mathrm{CF}^+}(q_d) + I_{\mathrm{F}^+}(q_d).$$

The electron and ion currents entering Eq. (2), in an orbit motion limited approximation are given by (see, e.g., Refs. 16 and 17)

$$I_e = -\sqrt{\pi/4\varepsilon_0}\, a^2 e (8 k_B T_e / \pi m_e)^{1/2} n_e \times \exp[e(\phi_d - \phi_{\mathrm{pl}})/k_B T_e], \tag{3}$$

$$I_{(j)} = \sqrt{\pi/4\varepsilon_0}\, a^2 e v_{(j)} n_{(j)} [1 - 2e(\phi_d - \phi_{\mathrm{pl}})/a m_{(j)} v_{(j)}^2], \tag{4}$$

where $\phi_d = -e|Z_d|/4\pi\varepsilon_0 a$ is the negative, with respect to the plasma potential ϕ_{pl}, potential of the spherical particle. Here, $v_{(j)} = [v_{(j0)}^2 + V_{Tj}^2]^{1/2}$, and $v_{(j0)}$ is the ion drift velocity in the plasma electric field, $V_{Tj} = [8 k_B T_{(j)} / \pi m_{(j)}]^{1/2}$ is the velocity of ion random motion, and $T_{e,(j)}$ and $m_{e,(j)}$ are the electron and ion temperatures and masses, respectively.

The ion velocities and currents strongly depend on the potential distribution in the plasma. For simplicity, we consider the particle charging in a plasma bulk, where the electric fields are normally weak so that $v_{(j0)} \ll V_{Tj}$ and microscopic ion currents are controlled by the ion thermal motion. We note that in the sheath/presheath regions this inequality can become incorrect due to strong electric fields in a plasma originating due to electron-ion charge imbalance in near-wall regions with strongly depleted electron density. Without losing generality, we can further assume the reference plasma potential to be zero. Otherwise, referring to the particle potential, we will further imply the particle surface potential with respect to the adjacent plasma. Later, we will also assume that the reactive species do not affect the particulate size, in other words, surface etching, adhesion and sputtering processes are neglected. Possible effects of such processes are briefly discussed in Sec. V.

III. EQUILIBRIUM PARTICLE CHARGE AND POTENTIAL

We now turn our attention to calculation of the equilibrium charge and electrostatic potential of particulates, the key parameters that control particle levitation, growth, and surface modification.[1] In the equilibrium state ($q_{d0} = \mathrm{const}$), the microscopic electron current balances the combined current of atomic and molecular ions, or

$$I_{e0}(q_{d0}) + \Sigma_{(j)} I_{(j0)}(q_{d0}) = 0,$$

which, after normalization, yields the following transcendental equation for the equilibrium dust charge Z_{d0}

$$(\tau_{\mathrm{CF}_3^+}/\mu_{\mathrm{CF}_3^+})^{1/2} \delta_{\mathrm{CF}_3^+} [1 + \Theta/\tau_{\mathrm{CF}_3^+}] + (\tau_{\mathrm{CF}_2^+}/\mu_{\mathrm{CF}_2^+})^{1/2} \delta_{\mathrm{CF}_2^+} [1 + \Theta/\tau_{\mathrm{CF}_2^+}] + (\tau_{\mathrm{CF}^+}/\mu_{\mathrm{CF}^+})^{1/2} \delta_{\mathrm{CF}^+} [1 + \Theta/\tau_{\mathrm{CF}^+}] + (\tau_{\mathrm{F}^+}/\mu_{\mathrm{F}^+})^{1/2} \delta_{\mathrm{F}^+} [1 + \Theta/\tau_{\mathrm{F}^+}] + (\tau_{\mathrm{Ar}^+}/\mu_{\mathrm{Ar}^+})^{1/2} \delta_{\mathrm{Ar}^+} [1 + \Theta/\tau_{\mathrm{Ar}^+}] = (1 - \chi_d) \exp(-\Theta), \tag{5}$$

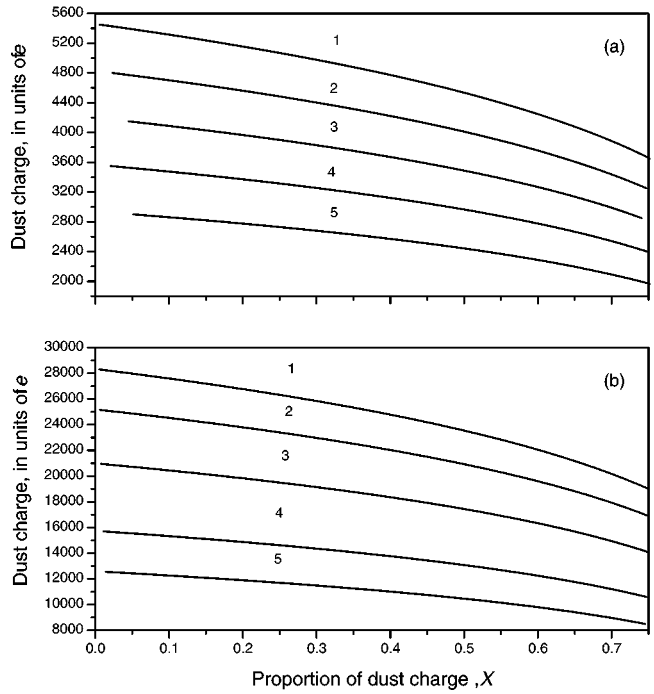

FIG. 1. Equilibrium charge of 1 (a) and 5 μm (b) particles as a function of dust charge proportion $X \equiv \chi_d$ in C_4F_8+Ar plasmas with $\tau_{CF_3^+} = \tau_{CF_2^+} = \tau_{CF^+} = 0.02$, $\tau_{F^+} = 0.025$, $\tau_{Ar^+} = 0.06$, $\delta_{CF_3^+} = 0.0125$, $\delta_{CF_2^+} = 0.0125$, $\delta_{CF^+} = 0.025$, $\delta_{F^+} = 0.005$, and $\delta_{Ar^+} = 0.945$. In diagram (a), curves 1–5 stand for $T_e = 2.6$, 2.3, 2.0, 1.7, and 1.4 eV, respectively. In diagram (b), curves 1–5 correspond to $T_e = 2.7$, 2.4, 2.0, 1.65, and 1.4 eV, respectively.

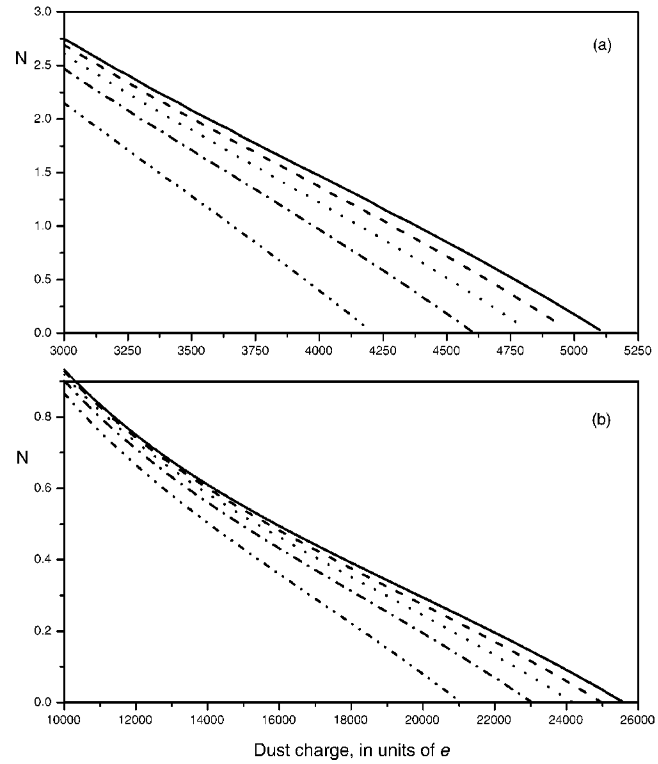

FIG. 2. Relative number density of 1 (a) and 5 μm (b) particulates $N \equiv N_d \times 10^4$ vs equilibrium charge for $T_e = 2.5$ eV, $\delta_{CF_3^+} = 0.0125$, $\delta_{CF_2^+} = 0.0125$, $\delta_{CF^+} = 0.05$, $\delta_{F^+} = 0.005$, $\delta_{Ar^+} = 0.92$, $\tau_{Ar^+} = 0.05$ (solid lines), $\tau_{Ar^+} = 0.04$ (dashed lines), $\tau_{Ar^+} = 0.03$ (dotted lines), $\tau_{Ar^+} = 0.02$ (dashed-dotted lines), and $\tau_{Ar^+} = 0.013$ (dashed-dotted-dotted lines). Other parameters are the same as in Fig. 1.

where $\delta_{(j)} = n_{(j)} / \Sigma n_{(j)}$ is the proportion of the number of ionic species (j) in the total number density of atomic and molecular ions, $\chi_d = |Z_{d0}| n_{d0} / \Sigma n_{(j)}$, $\tau_{(j)} = T_{(j)} / T_e$, and $\mu_{(j)} = m_{(j)} / m_e$. Note that the parameter $\Theta = e^2 |Z_{d0}| / 4\pi\varepsilon_0 a k_B T_e$ is a measure of ability of the plasma electrons with thermal energy $k_B T_e$ to overcome the potential barrier due to electrostatic repulsion by a negatively charged grain surface.[8]

Figure 1 shows the dependence of equilibrium negative charge of micron-size particulates on χ_d in C_4F_8+Ar plasmas with dominating argon content ($\delta_{Ar^+} = 0.945$). Similar situation has been reported for 2.66 Pa discharge in the inductively coupled plasma source with elevated input powers ($P_{in} \gtrsim 1.6$ kW).[13] We note that in such plasmas 1 μm size particles can typically acquire the negative charge with $|Z_d^{1\,\mu m}| \sim 2\times10^3 - 5\times10^3$. The 5 μm particles in fluorocarbon plasmas, in turn, can be charged up to $|Z_d^{5\,\mu m}| \sim 10^4 - 2.5\times10^4$. We note that the particulate charge diminishes with increase of χ_d, which is dictated by the overall charge conservation. Decrease of electron temperature strongly affects the equilibrium charge. In particular, lowering $k_B T_e$ from 2.6 to 1.4 eV results in diminishing of microscopic electron current onto the 1 μm particle, and the resulting charge becomes 1.6–1.8 times lower. The effect of electron temperature appears to be similar for 5 μm particles. Namely, variation of $k_B T_e$ from 1.4 to 2.7 eV yields an increase in average particle charge in 1.9–2.25 times.

The other factor that can affect the particulate charge, is temperatures of atomic and molecular ions. Figure 2 demonstrates how the temperature of argon ions T_{Ar^+} affects the relation between the relative dust number density $N_d = n_{d0} / \Sigma_{(j)} n_{(j)}$ and the equilibrium charge. The electron temperature and temperatures of other ions have been assumed invariable. From Fig. 2(a) one can notice that, at a given relative particulate number density, the variation of T_{Ar^+} from 0.033 to 0.125 eV modifies the equilibrium charge of up to 18%–32%. For larger particles [Fig. 2(b)], the effect of the T_{Ar^+} variation appears to be weaker. In fact, in the same range of argon temperatures, relative variation of $|Z_d^{5\mu m}|$ does not exceed 12%–22%. In both cases, lowering the argon temperature enhances the total ion current, and thus results in smaller absolute values of the dust charge. Note that in the case considered the scaling of ion currents with temperature can be approximated as $I_{(j0)} \sim T_{(j)}^{-1/2}$.

The other atomic and molecular ions originating in C_4F_8 plasmas also noticeably contribute to the particulate charging, which is depicted in Fig. 3. Different curves correspond to different temperatures of ions CF^+, CF_2^+, CF_3^+, and F^+. Temperatures of electrons and argon ions have been assumed fixed. As Fig. 3 reveals, the synchronized lowering of ion temperatures typically diminishes the particle charge of up to 10%. We note that the effect of the variation of temperatures of molecular ions, although feasible, is somehow weaker than that from argon ions. We remark that Fig. 3 has been plotted for higher proportions of molecular ions, which were reported for the experiments on microwave slot-excited C_4F_8+Ar plasmas at 2.66 Pa sustained with 0.5 kW microwave powers.[13]

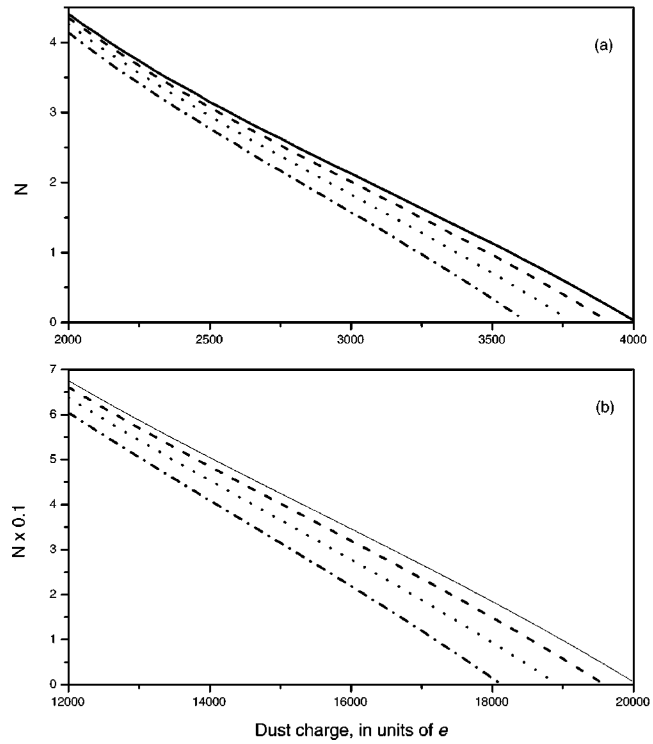

FIG. 3. Same as in Fig. 2 for $\delta_{CF_3^+}=\delta_{CF_2^+}=0.06$, $\delta_{CF^+}=0.18$, $\delta_{F^+}=0.05$, $\delta_{Ar^+}=0.65$, and $\tau_{Ar^+}=0.03$. Solid lines correspond to $\tau_{CF_3^+}=\tau_{CF_2^+}=0.064$, $\tau_{CF^+}=0.08$, $\tau_{F^+}=0.096$; dashed lines to $\tau_{CF_3^+}=\tau_{CF_2^+}=0.032$, $\tau_{CF^+}=0.04$, $\tau_{F^+}=0.048$; dotted lines to $\tau_{CF_3^+}=\tau_{CF_2^+}=0.016$, $\tau_{CF^+}=0.02$, $\tau_{F^+}=0.024$, and dashed-dotted lines to $\tau_{CF_3^+}=\tau_{CF_2^+}=\tau_{CF^+}=\tau_{F^+}=0.012$.

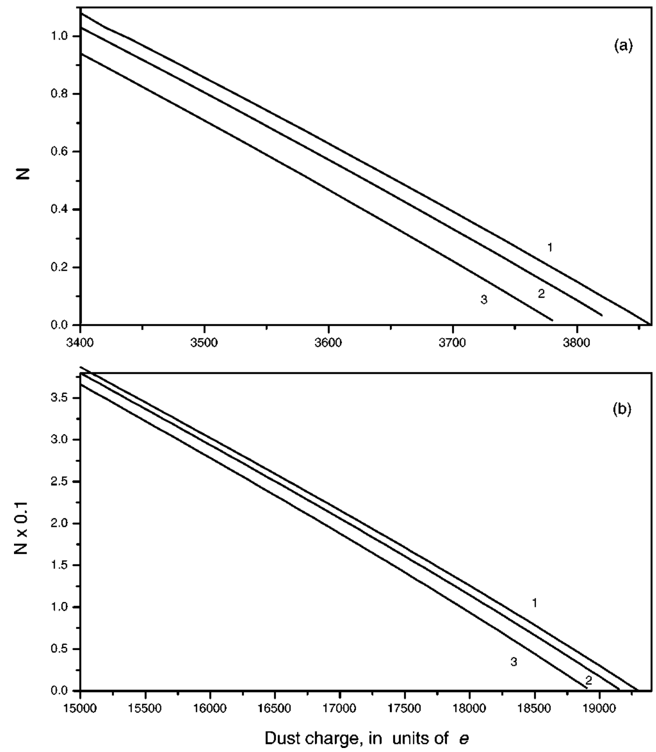

FIG. 4. Same as in Fig. 3 for $\delta_{CF_3^+}=0.06$, $\delta_{CF_2^+}=0.06$, $\delta_{F^+}=0.05$, $\tau_{CF_3^+}=\tau_{CF_2^+}=\tau_{CF^+}=0.02$, $\tau_{F^+}=0.024$, and $\tau_{Ar^+}=0.03$. Curves 1–3 correspond to $\delta_{CF^+}=0.05$ and $\delta_{Ar^+}=0.825$, $\delta_{CF^+}=0.12$ and $\delta_{Ar^+}=0.755$, and $\delta_{CF^+}=0.25$ and $\delta_{Ar^+}=0.625$, respectively.

Variation of ionic composition is also a factor affecting the equilibrium dust charge. However, as depicted in Fig. 4, this effect appears to be weaker. In particular, variation of proportion CF^+ component from 0.05 (curves 1) to 0.25 (curves 3) results in less than 3% diminishing of the equilibrium dust charge. In Fig. 4, the proportion of argon ions has been varied accordingly, whereas other parameters remained unchanged.

Figure 5 demonstrates how contributions of ion currents in the combined ion current $\xi_{(j)}=I_{(j)}/\Sigma_{(j)}I_{(j)}$ vary with the equilibrium particle potential. One can see that relative contributions of argon and CF^+ ions raise with the equilibrium particle potential. As can be seen from Fig. 5, contribution of argon ion current appears to be the highest, followed by contributions from molecular ions CF^+, CF_3^+, and CF_2^+. The relative proportion of fluorine ion current turns out to be very small. In particular, for 1 μm particles with $|Z_d|=3200$ the relative contributions of ionic species are $\xi_{Ar^+}\sim 0.597$, $\xi_{CF^+}\sim 0.225$, $\xi_{CF_3^+}\sim 0.105$, $\xi_{CF_2^+}\sim 0.066$, and $\xi_{F^+}\sim 0.007$, which remains similar for 5 μm particulates. In this example, the total proportion of CF_x^+, $x=1-3$ currents in the total ion current reaches 40%, which confirms the importance of molecular fluorocarbon ions in particulate charging process.

IV. CHARGE RELAXATION PROCESS

Earlier, we have assumed that the electron and ion currents are constant. However, inevitable power/pressure fluctuations in a discharge can result in certain modification of power and particle balance, which can be followed by variations in electron and ion currents $\tilde{I}_e$ and $\tilde{I}_{(j)}$. This will lead to inevitable fluctuations of the particle charge $\tilde{q}_d$. The dust charge relaxes afterwards, normally within time scale, which is much shorter than that for particle motion or surface modification.[9,10] We now calculate the time scale for the particulate charge relaxation in fluorocarbon etching plasmas and demonstrate that it is shorter than that in pure argon plasmas.

Assuming that $|\tilde{I}_{e,(j)}|\ll|I_{e0,(j0)}|$, and $|\tilde{q}_d|\ll|q_{d0}|$, one obtains

$$\frac{d\tilde{q}_d}{dt}+\nu_{ch}\tilde{q}_d=0, \tag{6}$$

where

$$\nu_{ch}=-\left(\frac{\partial I_e}{\partial q_d}+\Sigma_{(j)}\frac{\partial I_{(j)}}{\partial q_d}\right)_{q_{d0}}, \tag{7}$$

is the dust charge relaxation rate.

We note that the particle charge relaxation rate [Eq. (7)] strongly depends on background electron, atomic and molecular ion densities, which continuously vary in the process of dust charge fluctuation/relaxation. In fact, this process goes in such a way that the overall charge neutrality $n_{e0}+n_{d0}|Z_{d0}|=\Sigma n_{(j0)}$ is maintained at all times.[8] However, in many existing models of dust charging, the number densities of background electrons and ions were assumed unaffected (see, e.g., Refs. 9 and 10). In fact, this assumption is fairly

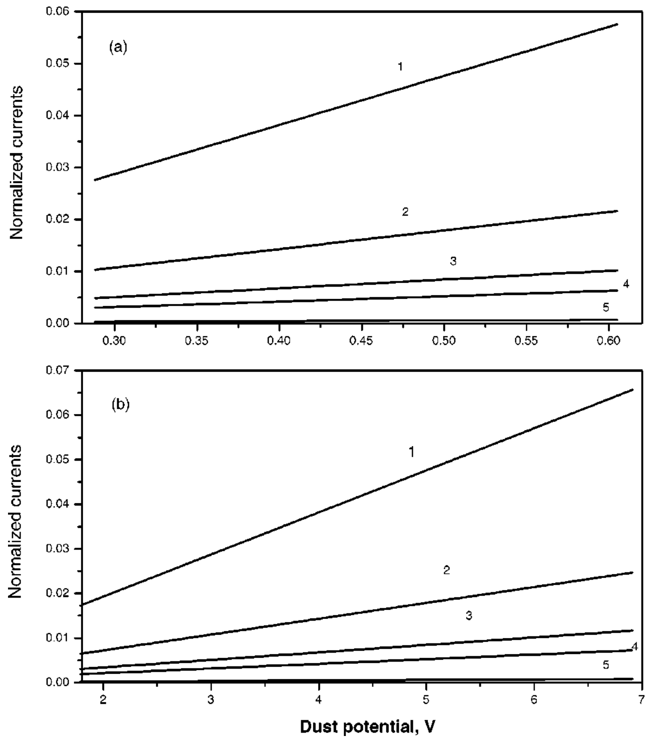

FIG. 5. Relative contributions of ion currents $\xi_{(j)}$ flowing onto 1 (a) and 5 μm (b) particles vs surface electrostatic potential in C_4F_8+Ar plasmas with $T_e = 1.5$ eV, $\tau_{CF_3^+} = \tau_{CF_2^+} = \tau_{CF^+} = 0.02$, $\tau_{F^+} = 0.024$, $\tau_{Ar^+} = 0.03$, $\delta_{CF_3^+} = 0.09$, $\delta_{CF_2^+} = 0.06$, $\delta_{CF^+} = 0.18$, $\delta_{F^+} = 0.005$, and $\delta_{Ar^+} = 0.665$. Curves 1–5 correspond to Ar^+, CF^+, CF_3^+, CF_2^+ and F^+, respectively.

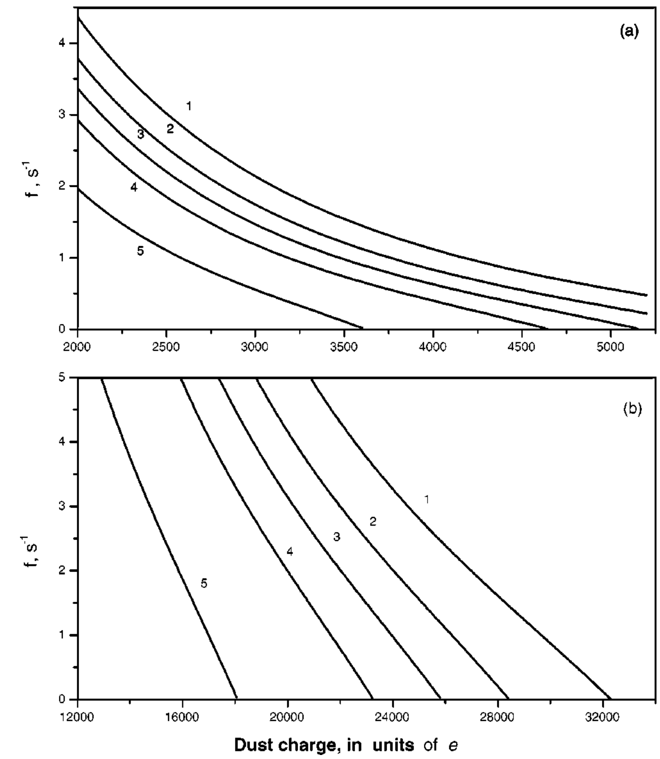

FIG. 6. Charge relaxation rates $f \equiv \nu_{ch} \times 10^{-8}$ of 1 (a) and 5 μm (b) particles as functions of equilibrium charge for $n_e \sim 4 \times 10^{11}\,\text{cm}^{-3}$, $\tau_{CF_3^+} = \tau_{CF_2^+} = \tau_{CF^+} = 0.02$, $\tau_{F^+} = 0.025$, $\tau_{Ar^+} = 0.05$, $\delta_{CF_3^+} = 0.0125$, $\delta_{CF_2^+} = 0.0125$, $\delta_{CF^+} = 0.05$, $\delta_{F^+} = 0.005$, and $\delta_{Ar^+} = 0.92$. Curves 1–5 are plotted for $T_e = 2.5$, 2.2, 2.0, 1.8, and 1.6 eV, respectively.

accurate if the proportion of negative charge residing on dusts is not high, that is, $\chi_d \ll 1$. Otherwise, the latter assumption becomes inconsistent with the overall charge neutrality, which requires that the number density of electrons or at least one of ionic species is affected by the particle charge variation. Physically, constant values of electron and ion number densities and the plasma charge neutrality can be simultaneously maintained in the process of particulate charge relaxation only by additional unspecified sources of electrons and ions.[8,17]

Here we shall calculate the micron-size particle charging rate without breaching the overall charge neutrality or invoking background particle sources and sinks. Instead, we assume that in the charge relaxation process, the number density of electrons and particle charge/potential vary simultaneously, while the number densities of atomic, molecular ions, and particulates remain constant.

Introducing the charge neutrality condition into Eq. (7), and accounting for the electron density variation with $\tilde{q}_d$, we obtain

$$\nu_{ch} = \frac{e|I_{e0}|}{4\pi\varepsilon_0 a k_B T_e}\Bigg[1 + \frac{1}{\Theta}\frac{\chi_d}{1-\chi_d} + \xi_{CF_3^+}(\tau_{CF_3^+} + \Theta)^{-1} + \xi_{CF_2^+}(\tau_{CF_2^+} + \Theta)^{-1} + \xi_{CF^+}(\tau_{CF^+} + \Theta)^{-1} + \xi_{F^+}(\tau_{F^+} + \Theta)^{-1} + \xi_{Ar^+}(\tau_{Ar^+} + \Theta)^{-1}\Bigg], \tag{8}$$

where I_{e0} is given by Eq. (3) after substitution of Z_{d0}. It is worthwhile to notice that the second term arises from the variation of background electron number density induced by particle charge fluctuation/relaxation process. The other terms can be obtained assuming $n_{e,(j)} = \text{const}$. However, should the inequality $\chi_d \ll 1$ be the case, the effect of the electron background density variation appears weak.

Figure 6 exhibits the charge relaxation rates of 1 and 5 μm particulates in a discharge dominated by argon atoms ($\delta_{Ar} \sim 0.92$, ICP sustained with $P_{in} \sim 1.6$ kW rf powers in 2.66 Pa C_4F_8+Ar discharge).[13] We notice that the dust charging rates are higher than those typically reported for argon discharges,[8] and normally exceed $10^8\,\text{s}^{-1}$. Indeed, neglecting the CF_x^+ ions and variations of the background electron density, one would obtain the charging rate almost one order of magnitude lower. Furthermore, this effect is crucial for higher ($\gtrsim$0.3–0.4) particulate charge proportions χ_d, featuring larger variations of the background electron density. In C_4F_8+Ar MSE plasmas with higher proportions of CF_x^+ ions the charge relaxation rates are even higher due to elevated contributions of currents of molecular ions. From Fig. 6 one can also notice that decrease of $k_B T_e$ from 2.5 to 1.6 eV diminishes ν_{ch} by 1.7–4 times.

V. DISCUSSION

Earlier, we used the simplified model for plasmas in octafluorocyclobuthane and argon mixture. Instead of analyzing the real cascaded electron-impact dissociation of molecule C_4F_8 into small fragment radicals, molecular and atomic ions, we actually substituted the real gas feed by the gas mixture $CF+CF_2+CF_3+Ar$, which is equivalent to the decomposition reaction $C_4F_8 \rightarrow CF+2CF_2+CF_3$, which, in fact, may not necessarily occur through any single-step dissociation event. The actual primary and secondary reactions in C_4F_8 plasmas can be found, e.g., in Refs. 14 and 18, which, in particular, suggest that electron-impact reactions leading to formation of CF, CF_2, and CF_3 radicals are characterized by larger cross sections and lower thresholds than that for formation of other radical species. Moreover, reasonability of such a simplification is evidently supported by experimental data on ionic composition in inductively coupled and microwave slot-excited C_4F_8+Ar plasmas at 2.66 Pa.[13] Above all, similar ionic composition has been successfully applied for modeling the electron energy distribution functions in fluorocarbon discharges.[15]

It is instructive to note that fluorine atoms and other fluorocarbon radicals can attach electrons and become negative ions. In particular, recent laser photodetachment experiments in plasmas of C_4F_8 and Ar gas mixtures suggest that in high-density plasmas the total number density of negative ions can be comparable with that of other discharge species.[19] Physically, it is not expected that negative ions will affect the particulate charging process due to strong electrostatic repulsion by the dusts and negligibly weak collection currents.[16] However, should the proportion of negative ions be comparable with that of the plasma electrons, one can expect microscopic electron currents onto the grains be somewhat depleted. Thus, the effect of negative ions on particulate charging deserves separate attention and detailed data on composition of electronegative fluorocarbon plasmas is warranted.

In our consideration we have also sidestepped the kinetics of fluorocarbon radicals, as well as that of fluorine and other neutrals. Indeed, the primary concern in this article are the electrostatic charging processes of micron-size particulates by microscopic currents of plasma electrons and ions, which were assumed unaffected by neutrals. This assumption is usually accurate in weakly collisional ($\omega \gg \nu_{en}, \nu_{in}$) plasmas, where ν_{en} and ν_{in} are the electron-neutral and ion-neutral collision rates, and ω is the generator frequency.[7] One can show that the latter inequality is easily satisfied for parameters of microwave (2.45 GHz) experiments at 2.66 Pa pressure,[13] whereas it is not apparent for lower-frequency (13.56 MHz) case, when the rf can be of the same order, or even less than the rates of electron-neutral and ion-neutral collisions. However, calculating the electron (3) and ion (4) currents we have assumed that the effect of electron and ion drifts (which are affected by collisions with neutrals) in electrostatic fields in the plasma, is small compared with that from electron/ion random motion. This is well justified in a plasma bulk, where electrostatic fields are weak enough and do not noticeably affect the particulate charging process.[17] And since the charge proportions on dusts and plasma electrons can be comparable, the present study also implies that overall charge/density fluctuations affect the particulate cloud in an essentially uniform and charge-neutral plasma bulk. Should the particles be levitated in the near-sheath regions with relatively strong electric fields, the charging scenario could be different. Physically, the effects of directional ion flows and collisions with atoms/radicals will come into play, and the combined ion current can strongly be enhanced. On the other hand, the electron charging current will be lower due to significant depletion of electron number density in near-wall regions. The balance between the electron and ion currents will thus be modified so that the average negative charge on particulates can be different than in a plasma bulk.

The other issue is the effect of active species on the equilibrium charge and potential of individual particles. Physically, in etching plasmas, the size and shape of fine particles can be dynamically varied through surface sputtering, chemical etching processes, which diminish the particle size. Meanwhile, the radicals CF, CF_2, and CF_3 can stick to the particle surface and form thin films on its surface. However, because of relatively low potential of particulates with respect to adjacent plasma (Fig. 5), surface sputtering effects can be neglected. By assuming the particle size invariable, we have thus presumed that chemical etching and thin film deposition processes dynamically balance each other. Furthermore, the surface modification processes occur at time scales much larger than that for particle charging, and cannot affect the results of current consideration. Conversely, consideration of surface modification of fine particles would be inaccurate without taking into account the variation of equilibrium dust charge and potential with particle size. We note that this process requires specific models for gas-phase and surface kinetics and will be the subject of forthcoming studies.

The results of Figs. 1–4 enable us to rate the factors affecting the equilibrium charge of micron-size particles in C_4F_8+Ar plasmas. The variation of the electron temperature is perhaps the most important factor for the equilibrium particle charge (Fig. 1). The effect of temperatures of atomic and molecular ions appears somehow weaker (Figs. 2 and 3). As Fig. 4 shows, variation of the ion number density composition does not strongly affect the particulate charge. Thus, the equilibrium particle charge/potential, usually very sensitive to the electron temperature variation, can also efficiently be controlled by varying the temperatures of atomic and molecular ions. We note that the effect of positive ionic species on particulate charging process is enhanced by diminishing $T_{(j)}$ but also appears to be quite feasible at higher ion temperatures ($T_{(j)} \sim 0.1T_e$).

It should be emphasized that the total current of fluorocarbon ions onto the particulates appears to be comparable to that of argon ions. In particular, in low-power microwave slot-excited discharges it can be as high as 40%. Furthermore, the contribution of CF^+ current alone is typically of the order of 20%, even in discharges in 90% Ar and 10% C_4F_8 gas mixture. However, as the results of our study suggest, the argon ion current remains the dominant factor in setting-up the equilibrium particulate charge. This fact can be used for zero-order estimates of the dust-to-plasma electrostatic potential in situations when the initial argon inlet dominates while the exact composition of fluorocarbon active species is not known. Nonetheless, contribution of molecular ions CF_x^+ appears to be important, and in some cases can modify the equilibrium particulate charge of up to 30%–40%. Likewise, the consideration of fine particle surface modification will be incomplete without physically feasible models of interaction of fluorine atoms, fluorocarbon ions, and radicals with the particle surface.

Meanwhile, the dust charge relaxes within time scales which are much shorter than that for particle surface modification. This process does not affect the equilibrium particulate potential or average charge. However, the charge relaxation process introduces relatively high dissipation of rf power in a discharge, with the rates comparable or even higher than the driver frequency.[20] Hence, the rf power deposition processes in a discharge can be affected such that the power and particle balance processes can be dramatically distorted. In particular, increase of the charge carried by particulates χ_d is accompanied by depletion of the electron number density and results in somehow higher electron temperatures in the plasma bulk.[20] This is confirmed by a common observation that dust-contaminated states of low-pressure gas discharges feature higher values of T_e than ''pure'' ones.[1] Hence, the electron-impact ionization rates can noticeably be enhanced, which can, in turn, modify the microscopic electron/ion currents onto the particles. Such an effect can be regarded as an illustration of the nonlinear (rf power dependent) self-consistent response seeking to restore the equilibrium state.[20] Furthermore, if χ_d is high enough, discharge instabilities, mode jumps, and possibly a major disruption can be the consequencies of the charge relaxation process.[1]

In the case considered, the particle charge relaxation rates appear to be very high, and typically exceed $10^8\,\mathrm{s}^{-1}$. This turns out to be a very serious factor in the frequency range <100 MHz, which becomes increasingly attractive for materials processing applications. First, instantaneous fluctuations of currents of fluorocarbon ions significantly enhance the charge relaxation rate. The other factor that comes into play at higher proportions of dusts ($\chi_d \sim 1$) is the variation of the background electron number density, which accompanies the particle charging/charge relaxation processes. For instance, as follows from Eq. (8), at $\chi_d = 0.5$, and $\Theta \sim 2.25$, the contribution of the electron number density variation effect to the particle charge relaxation rate can be as high as 45%.

By accounting for the effect of the background electron number density variation with the particle charge we overcome the limitations of the existing variable-charge approach.[9,10] In particular, the particulate charge variation is instantaneously accompanied by fluctuations of number densities of plasma electrons and ions, and results in a distortion of the particle and charge balance in the plasma. In many existing models, deviations of background electron/ion number densities from equilibrium values are usually assumed to be compensated by unspecified uniformly distributed particle sources and sinks.[8] In reality, however, fine particle charging must affect the electron/ion number densities in the adjacent plasma. Earlier, we have assumed that the number density of the ions and particulates remain constant, but allowed for variations in the electron density and particulate charge, which has actually been observed in many dust-contaminated plasmas.[8] We pinpoint that the actual charging rate of micron-size particles appears to be higher than that obtained using the conventional assumption $n_{e,(j)} = \mathrm{const}$. It should also be emphasized that in situations when particle clouds actually absorb most of the plasma electrons ($n_{d0}|Z_{d0}| \gg n_{e0}$), occurring frequently in plasma-wall regions, the commonly used dust charging rate would be incorrect, and Eq. (8) has to be used instead. This circumstance should be carefully accounted for in forthcoming models of power and particle balance in discharges contaminated by fine particles levitating in sheath/presheath regions.

VI. CONCLUSION

We have studied the electrostatic charging of micron-size particulates in discharges in $C_4F_8 + Ar$ gas mixtures frequently used for ultrafine and highly selective etching applications. The average charge on an individual particle is controlled by a combination of microscopic electron and ion currents, the latter comprising the currents of atomic (Ar^+ and F^+), and molecular ions (CF_3^+, CF_2^+, and CF^+). The data on plasma composition and other parameters have been taken from the experiments on inductively coupled and microwave slot-excited plasmas of $10\%\,Ar + 90\%\,C_4F_8$ gas mixture at 2.66 Pa.[13] The effect of electron/ion temperatures and ion composition on the average dust charge has been studied. The estimates reveal that the variation of proportion and composition of molecular ionic species does not cause any significant effect on the particulate charging/charge relaxation processes. However, molecular ion temperatures appear to be a factor affecting the equilibrium particle potential. Indeed, an increase of temperatures of molecular ions results in a 10% raise in absolute values of the particulate charge/potential. Furthermore, the combined $CF^+ + CF_2^+ + CF_3^+$ current can constitute up to 40% of the total ion current onto the particle. Meanwhile, CF^+ molecular ions appear to be the most important contributors, responsible for more than 20% of the total ion current.

It has also been shown that fluorocarbon dusty plasmas exhibit high charge relaxation rates, typically exceeding $10^8\,\mathrm{s}^{-1}$ for more-than-a-micron particulates. This can definitely be attributed to impacts of fluorocarbon molecular ions, in particular CF^+, as well as to variations of the background electron number density which accompany particulate charging/charge relaxation processes. The account for the background electron density variation makes possible to maintain the overall charge neutrality in the plasma without any external particle sources or sinks implied in many existing models of dust charging. In our study, the charging rates have been calculated assuming the overall charge neutrality, regulated by simultaneous variations of the dust charge and the electron number density.

Finally, we emphasize that the results of this work are important for optimizing the surface modification processes of micron-size particles. The improved models should include elements of particle and power balance in the discharge, sheath effects, as well as surface kinetics. The results on some of the earlier effects are outside the scope of this article and will be reported elsewhere.

ACKNOWLEDGMENTS

This work was supported by the Japan Society for the Promotion of Science, Australian Research Council, Toshiba Corp., Nissin Inc., and Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture. Fruitful discussions with S. V. Vladimirov, H. Toyoda, K. Nakamura, and T. Ishijima are kindly appreciated.

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